

**UNITED STATES PATENT APPLICATION FOR:**

**COPPER REPLENISHMENT FOR COPPER PLATING WITH INSOLUBLE ANODE**

**INVENTORS:**

**NICOLAY Y. KOVARSKY**

**DMITRY LUBOMIRSKY**

**ALEXANDER F. HOERMANN**

**SARAVJEET SINGH**

**ATTORNEY DOCKET NUMBER: AMAT/8451/CMP/ECP/RKK**

**CERTIFICATION OF MAILING UNDER 37 C.F.R. 1.10**

I hereby certify that this New Application and the documents referred to as enclosed therein are being deposited with the United States Postal Service on **October 21, 2003**, in an envelope marked as "Express Mail United States Postal Service", Mailing Label No. **EV351032102US**, addressed to: Commissioner for Patents, Mail Stop PATENT APPLICATION, P.O. Box 1450, Alexandria, VA 22313-1450

*John Paul F. Cherny*  
Signature  
*John-Paul F. Cherny*  
Name  
*10/21/2003*  
Date of signature

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

**COPPER REPLENISHMENT FOR COPPER PLATING WITH INSOLUBLE ANODE**

**BACKGROUND OF THE INVENTION**

**Field of the Invention**

[0001] Embodiments of the invention generally relate to a metal plating apparatus and process, namely for the replenishment of chemical components used to electroplate copper.

**Description of the Related Art**

[0002] Semiconductor substrates can be plated with copper by electroplating or electroless plating processes. During the electroplating, an anode is usually placed into an electrolyte solution and the substrate is conductively coupled to a cathode. As current flows, dissolved copper ions from the electrolyte solution are reduced and plated (or deposited) on the surface of the substrate as copper metal. Traditionally, the anode is made from consumable copper metal and is continuously oxidized to provide copper ions to the plating process. Due to the consumption of the copper anode, the dimension of the copper anode is changed. Therefore the directional electrical fields produced by the anode also change accordingly. This alteration in the electric field presents a challenge to precisely control the electroplating process, especially within vias with high aspect ratios.

[0003] Another electroplating process utilizes an inert or stable anode in place of a consumable anode. The use of an inert anode provides excellent control for precision plating since the anode is not consumed during the plating process. However, the inert anode does not supply a source of copper into the electrolyte solution. As the copper ions are reduced and plated from the electrolyte solution to the substrate surface, the copper ion concentration in the electrolyte solution is diminished. Therefore, as the plating process progresses, a copper source, namely copper ions, must be added to the electrolyte solution in order to continue the plating process. Copper sources are generally chosen from a variety of copper salts that include copper sulfate, copper hydroxide, copper oxide and copper phosphate.

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

[0004] United States Patent Number 5,516,414 teaches a method to maintain an alkaline copper plating solution with a desired concentration of copper ions and hydroxide ions. The '414 patent discloses adding copper hydroxide powder from a conduit to an alkaline, pyrophosphate solution in a dissolving tank. Once the solution has been heated and agitated to insure that the copper hydroxide has been dissolved, the pyrophosphate solution is transferred via a pump to the plating solution. The plating solution is monitored with a meter and maintained with a basic pH between 7 and 10 by adding the alkaline, pyrophosphate solution. Though the addition of copper hydroxide powder is adequate in the realm of electroplating wires, this technique is unacceptable in a clean environment, such as a semiconductor fabrication room equipped to plate substrates. The dumping of a powdery precursor into a solution would present contamination issues for semiconductor processing in a cleanroom environment.

[0005] United States Patent Number 5,997,712 realizes the shortcomings of the '414 patent as applied to a cleanroom. The '712 patent avoids dumping the powdery precursor and teaches a method to replenish copper ions in a plating solution with the apparatus depicted in Figure 1A. The anolyte flows from the top of canister 2, through a porous cartridge 4 and into a hollow cavity 6 before flowing out the bottom of canister 2. The cartridge 4 includes a filter element that encompasses the powdery copper source. Therefore, the anolyte flows through the canister 2 and is enriched by copper ions via absorbing the copper source.

[0006] However, as illustrated in Figure 1B, the anolyte can flow into cartridge 4 and form different phases of anolyte/copper source. The depleted anolyte 8 enters the cartridge 4 from above and flows downwardly to form a suspension 9 of anolyte/copper source. As the suspension 9 flows towards the bottom of the cartridge 4, the suspension densifies, forming a viscous cake 10 at the bottom of the cartridge 4. Throughout the formation of cake 10, the flow of anolyte lessens and copper ions cease to be consistently replenished in the anolyte. Therefore, longer plate times reduce substrate throughput with this decrease of the copper

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

concentration. Also, in the case when copper hydroxide is used as a copper source, the reduction in the hydroxyl ion addition lowers the pH of the anolyte.

[0007] Therefore, there is a need for an apparatus and method to replenish chemical compounds within an electrolyte solution in a consistent and reliable manner.

**SUMMARY OF THE INVENTION**

[0008] In one embodiment, the invention generally provides an apparatus for dispersing chemical reagents to a plating solution including a tank for containing the plating solution and a cartridge in fluid communication with the tank, wherein the cartridge has an input and an output. The apparatus further includes at least one shelf contained inside the cartridge. The at least one shelf may be impermeable and may extend between the input and the output such that the chemical reagent rests on the at least one shelf.

[0009] In another embodiment, the invention generally provides an apparatus for dispersing a chemical reagent to a plating solution comprising a tank for containing the plating solution and a vertical cartridge in fluid communication with the tank. A lower portion of the vertical cartridge includes an inlet and an injector port and an upper portion of the vertical cartridge includes an outlet and a manifold. The chemical reagent is positioned between the inlet and the outlet.

[0010] In another embodiment, the invention generally provides a method for dispersing a chemical reagent to a plating solution including flowing the plating solution from a tank through an input of a cartridge, wherein the cartridge comprises a chemical reagent disposed on at least one shelf. The plating solution flows across the chemical reagent to enrich the plating solution with the chemical reagent, whereas the chemical agent is dissolved or suspended within the plating solution. The enriched plating solution flows from the cartridge through an output to the tank.

[0011] In another embodiment, the invention generally provides a method for monitoring and controlling a pH setting of a plating solution in a tank including

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

determining a pH of the plating solution with a pH meter, transferring an aliquot of the plating solution to a vessel and pressurizing the vessel with a gas to transfer the aliquot to a cartridge. The cartridge includes an injector, a chemical reagent and a manifold. The aliquot passes through the injector, which enriches the aliquot with a portion of the chemical reagent and the enriched aliquot transfers through the manifold to the plating solution in the tank. A second pH of the plating solution is determined with the pH meter and compared with the pH setting. Enriched aliquots are transferred repeatedly to the plating solution until the second pH is equivalent to the pH setting.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0012] So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0013] Figures 1A-B show a cartridge inside a canister as used in the related art;

[0014] Figure 2 shows a flow diagram for a two-sectional electrochemical cell with catolyte and anolyte;

[0015] Figure 3 shows a longitude sectional view of a cartridge with horizontal shelves;

[0016] Figures 4A-C show cross-sectional views of cartridges with a variety of shelves;

[0017] Figures 5A-C show cartridge placements into an anolyte loop;

[0018] Figure 6A shows a vertical sectional view of a cartridge with a bottom injector;

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK

Express Mail No.: EV351032102US

[0019] Figure 6B shows a fragmentary vertical sectional view of a portion of the embodiment of Figure 6A;

[0020] Figure 7 shows a schematic diagram of a plating system incorporating one embodiment of a cartridge with a bottom injector;

[0021] Figure 8 is a diagram illustrating the timing sequence of valve operation during a plating process;

[0022] Figure 9 shows another embodiment of a cartridge with a bottom injector incorporated into a plating system; and

[0023] Figure 10A-B show embodiments of injector systems including rotatable cups.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

[0024] The present invention comprises apparatuses and methods to replenish chemical compounds in plating solutions in a consistent and reliable manner. The present invention overcomes the shortcomings of the related art as described in the background and illustrated in Figure 1, mainly, by not blocking anolyte flow with cake formations. Therefore, by utilizing the various embodiments of the apparatuses and methods of the present invention, each substrate experiences more consistent plating times and anolyte chemical concentrations.

[0025] Embodiments of the present invention are useful in a variety of plating systems, including electroplating and electroless plating systems. Further, various embodiments are also applicable to electroplating with soluble anodes and with insoluble anodes. Figure 2 shows a schematic arrangement of an electroplating system with a cell 11 containing an insoluble anode 12. The insoluble anode 12 is made from relatively inert materials, such as platinum, titanium, titanium with a Pt-coating, palladium, nickel, stainless steel and/or carbon. The material of the insoluble anode 12 is generally configured to withstand the various process conditions involved while plating to a wafer or substrate 14. Process conditions may

## PATENT

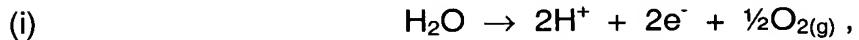
Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

have acidic or basic pH, oxidative/reductive potentials and an assortment of chemical compounds throughout the solution. In one embodiment, the insoluble anode 12 endures process conditions such as acidic plating solutions and an oxidative potential. The substrate 14 is attached to the cathode 13, usually by a contact ring, pins, and the like (not pictured).

[0026] The insoluble anode 12 and the cathode 13 are separated by a membrane 16 extending through cell 11. The membrane 16 is an electroconductive membrane, such as an ion-exchange membrane, nano-filtration membrane, ultra-filtration membrane and others known in the art. The portion of the cell 11 containing the cathode 13 is in fluid communication with the catolyte tank 17 to recirculate the catolyte within. The catolyte is a mixture of compounds that may include, for copper plating, sulfuric copper plating electrolyte or pyrophosphoric copper plating electrolyte. A sulfuric copper plating electrolyte will generally include a mixture of copper sulfate, sulfuric acid and various organic and inorganic additives including suppressors, accelerators, levelers and brighteners. Catolyte may pass through a diffuser 15 and be more evenly distributed while flowing to the substrate 14.

[0027] The portion of the cell 11 containing the insoluble anode 12 is in fluid communication with the anolyte tank 18 and recirculates the anolyte within. For copper plating, the anolyte is a solution containing copper ions, often derived from dissolved copper salts, such as copper sulfate. Other copper ion sources include copper hydroxide, copper carbonate, copper oxide and copper phosphate.

[0028] Under copper plating electrolysis, the half reaction in scheme (i) occurs on the insoluble anode 12:



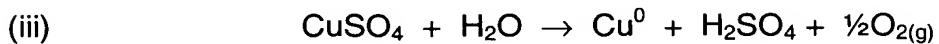
while  $\text{Cu}^{2+}$  ions migrate through the membrane 16 from the anolyte to the catolyte and are reduced according to the half reaction shown in scheme (ii):



PATENT

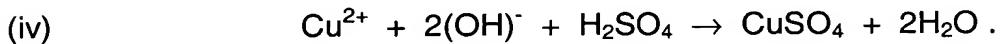
Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

The combined half reactions are represented in reaction scheme (iii):



Therefore, as the electroplating process proceeds, the anolyte becomes depleted of copper ions due to the precipitation of metallic copper as well as more acidic due to the production of sulfuric acid. Also, water is consumed making the electrolyte more concentrated.

[0029] The sulfuric acid formed in the anolyte penetrates through the membrane 16 and contaminates the catolyte. The sulfuric acid lowers the pH of the catolyte. More acidic catolyte is not desirable because the membrane loses ion selectivity between protons and copper ions. The loss of the membrane selectivity permits protons to compete with copper ions while penetrating the membrane, therefore, unbalancing the catolyte chemical concentration. To prevent the lowering of the pH of the catolyte, an alkaline compound is added. Copper hydroxide consists of a copper ion source as well as a hydroxyl source and will neutralize formed sulfuric acid, as shown by the reaction scheme (iv):



Therefore, schemes (iii) and (iv) are combined and the proportional amount of copper hydroxide is added to the anolyte. The summed reaction is depicted in scheme (v), namely copper is consistently deposited while water and oxygen are formed as byproducts, such as:



[0030] Figure 3 shows a longitudinal sectional view of an embodiment of a cartridge system 20 including a cartridge 22 containing one embodiment of shelves 24 of the invention. The shelves 24 are vertically spaced apart and extend longitudinally between input 32 and output 34. The shelves 24 may number in a range from about 1 to about 50, though preferably from about 2 to about 10. Figures 3 and 4A illustrate four horizontal substantially flat top shelves. The cartridge 22 and

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK

Express Mail No.: EV351032102US

the shelves 24 may be made from an assortment of materials, such as plastics or metals, including stainless steel, aluminum, titanium, nickel-coated steel and various alloys, amongst others.

[0031] Chemical reagents 26 are distributed across each of the shelves 24. The chemical reagents are exposed to plating solution 28 (depicted with arrows) flowing through the cartridge 22. The plating solution 28 enters the cartridge at least partially depleted of various chemical components, but is enriched by flowing over the chemical reagents 26 contained within the cartridge 22. The enriching process includes the dissolving and/or suspending of chemical reagents 26 within the plating solution 28. The chemical reagents 26 usually have a solid state of matter (e.g., powder, pellets, crystalline), but could also be a viscous liquid or a suspension. Therefore, enriched plating solution 29 emerges from the output 34. A progressive and consistent transformation or enrichment of the plating solution occurs as plating solution 28 flows across chemical reagents 26. In one example, the shelves 24 are impermeable to liquids (e.g., metal plate with no holes or no porosity), so the plating solution 28 passes along and not through the shelves 24. In another example, the shelves 24 are permeable to liquids, such as ceramic or mesh, so the plating solution 28 passes along and/or through the shelves 24.

[0032] Chemical reagents 26 are compounds or mixtures of compounds selected for the process requirements of the plating solution. Plating solutions include electroless plating solutions and electroplating solutions, wherein the latter is usually the anolyte or the catolyte. Electroplating systems are utilized to deposit materials such as copper, zinc, cadmium, nickel and other metals. In one preferred embodiment, the plating solution is an anolyte within an electroplating system used to plate copper.

[0033] Chemical reagents 26 useful for copper ion replenishment in a plating solution include copper hydroxide, copper oxide, copper carbonate, copper sulfate and copper phosphate and combinations thereof, preferably copper hydroxide. Generally, plating solutions, enriched or depleted, have a copper ion concentration in a range from about 5 g/L to about 70 g/L.

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

[0034] Chemical reagents 26 are also used to replenish plating solutions of other depleted compounds and ions. In one embodiment, chemical reagents are used to control the pH of the plating solution. The pH of the solution can be raised or lowered by adding a basic or acidic compound, respectively. Chemical reagents 26 for replenishing hydroxyl ions to increase the pH include copper hydroxide, ammonium salts, sodium hydroxide, potassium hydroxide, lithium hydroxide, cesium hydroxide, magnesium hydroxide, calcium hydroxide, amongst others, and combinations thereof. Therefore, in one embodiment, copper hydroxide is used to replenish copper ions and hydroxyl ions.

[0035] Porous material 25 is optionally placed at either or both ends of the cartridge 22 and include porous plastics, metals, ceramics, filters, frits, membranes, wool (e.g., glass or metal), packed inert media (e.g., silica or alumina) and the like. Generally, the porous material has pores that are penetrable for enriched plating solution (suspensions), but prevents chemical reagents 26 from uncontrollably passing through the cartridge 22. The porous material has pores with a diameter in the range from about 10  $\mu\text{m}$  to about 2,000  $\mu\text{m}$ .

[0036] Figures 4A-C show cross-sectional views of cartridge system 20 with a variety of geometries for cartridges and shelves. Figure 4A shows the four flat shelves 24 of Figure 3 as described above. Figure 4B shows shelves with longitudinal grooves 36. The grooves 36 further segregate the chemical reagents 26 into various rows running along each shelf. Figure 4C shows a cylindrical cartridge 37 containing tubular shelves 38. Tubular shelves 38 also hold chemical reagents 26 in segregated rows. The shelves distribute (*i.e.*, provide more surface area) chemical reagents 26. Time exposure between the plating solution and the chemical reagent varies the degree of enrichment the plating solution endures. Therefore, the flow of the plating solution through cartridge 22 varies in a range from about 0.5 L/min to about 10 L/min, depending on the bath volume and performance.

[0037] The flow of the plating solution is maintained due to part of headspace 30 provided above the top surface of the chemical reagents 26. Generally, headspace 30 has a height in the range from about 1 cm to about 50 cm, preferably from about

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

5 cm to about 30 cm. Headspace 30 changes throughout the process with respect to time, since the chemical reagents 26 are consumed by the plating solution and the height of headspace increases. Also, headspace 30 changes throughout the process with respect to certain segments along the shelves. Besides consumption, chemical reagents 26 also migrate and erode along the shelves.

[0038] In several examples, as depicted in Figures 5A-C, cartridge system 20 is placed into anolyte loops with various configurations. In one embodiment, Figure 5A shows cartridge system 20 placed into a single anolyte loop. As anolyte requires replenishment of chemical reagents (e.g., Cu<sup>2+</sup> or OH<sup>-</sup>), pump 120 draws depleted anolyte from the anolyte tank 110. With control valve 130 open, pump 120 pushes the depleted anolyte through cartridge system 20. The anolyte emerges from the cartridge system 20 enriched with the specific chemical reagents required for the plating process (e.g., Cu(OH)<sub>2</sub>). Upon exiting the cartridge system 20, anolyte flows to the electroplating cell 100, where the plating process commences, forming depleted anolyte, which is transferred back to the anolyte tank 110. This cycle resumes as the anolyte is recirculated throughout the anolyte loop.

[0039] In another embodiment, Figure 5B shows cartridge system 20 placed into an anolyte loop also including a bypass line. The bypass line is useful when the anolyte is only partially depleted of the necessary chemical reagents. Though depleted anolyte will contain some essential chemical reagents, the concentration of the reagents is too low and affects the plating process. However, partially depleted anolyte is suited to be recirculated and used in the electroplating process prior to being enriched by cartridge system 20. Depleted or partially depleted anolyte is determined per process parameters. As anolyte requires replenishment of chemical reagents (e.g., Cu<sup>2+</sup> or OH<sup>-</sup>), pump 120 draws depleted anolyte from the anolyte tank 110. With control valve 130 open and control valve 135 closed, pump 120 pushes the depleted anolyte through cartridge system 20. The anolyte emerges from the cartridge system 20 enriched with the specific chemical reagents required for the plating process (e.g., Cu(OH)<sub>2</sub>). Upon exiting the cartridge system 20, anolyte flows to the electroplating cell 100. However, with control valve 130 closed

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK

Express Mail No.: EV351032102US

and control valve 135 opened, pump 120 pushes the partially depleted anolyte through a bypass around the cartridge system 20 and directly to the electroplating cell 100. Upon the commencement of the plating process, depleted anolyte is transferred back to the anolyte tank 110. This cycle resumes as the anolyte is recirculated throughout the anolyte loop.

[0040] The anolyte cycle system depicted in Figure 5B has an advantage over the system depicted in Figure 5A due to the cartridge bypass line, namely, more control of the supplemental chemical reagent addition. Since the system of Figure 5B has the bypass line, anolyte is recirculated with the option to pass through cartridge system 20. For any of the anolyte loops depicted in Figures 5A-C, the capacity of anolyte tank 110 can be increased to slow the anolyte dilution from the addition of depleted anolyte coming from cell 100.

[0041] The system depicted in Figure 5C includes several anolyte loops linked together via the anolyte tank 110. One loop includes the electroplating cell 100 in fluid communication with the anolyte tank 110. Pump 120 circulates the anolyte within this loop. However, an auxiliary loop is also linked with the anolyte tank 110. The auxiliary loop includes the cartridge system 20 connected to a control valve 134 and a pump 125. In one aspect, pump 125 is a high-pressure pump. Also incorporated to the auxiliary loop is a bypass line managed by control valve 132. Therefore in one aspect, with control valve 134 opened and control valve 132 closed, anolyte can be circulated between the anolyte tank 110 and cartridge system 20 to be enriched with chemical reagents, while the anolyte is circulated between the anolyte tank 110 and the electroplating cell 100. In another aspect, control valve 134 is closed while control valve 132 is opened and cartridge system 20 does not replenish the supplemental chemical reagents to the system.

[0042] In another embodiment, Figures 6A-B show cartridge 40 as a vertical vessel in which a lower portion of the interior of the vessel expands upwardly to form an inverted conical bottom 42. The cartridge 40 includes top 39 as a portion of housing 41, both made from an assortment of materials, such as plastics or metals,

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

including stainless steel, aluminum, titanium, nickel-coated steel, various alloys amongst others.

[0043] At the base of the conical bottom 42, an injector 43 is positioned in a vertical arrangement. The conical bottom 42 collects the settling chemical reagents 26 by gravitational forces. This settling process maintains the chemical reagents 26 in contact with the injector 43. The injector has an input 45 that is in fluid communication with the electroplating system. Depleted electrolyte 28 combined with or without gas (e.g., air) passes through the input 45 and is introduced into the cartridge 40 through at least one output 47 of injector 43. In one embodiment, there are multiple outputs 47 in a single injector 43. The orifice that provides the output 47 generally has a diameter in the range from about 0.1 mm to about 1 mm. As depicted in Figure 6B, outputs 47 are less than normal (*i.e.*, <90°) relative to the plane of the axis of the conical bottom 42. That is, the outputs 47 generally point downward, towards the conical bottom 42 and extend through the sides 48 of injector 43. However, in one embodiment (not shown), the channels are normal or pointing upward, but have an optional flap in order to keep chemical reagent from descending into the outputs.

[0044] Plating solution or electrolyte is administered into the cartridge 40 through the injector 43. Chemical reagents 26 are disposed within the cartridge 40, so the electrolyte travels through the chemical reagents 26 and into a headspace 49. An under pressure (e.g., vacuum system) and/or an over pressure (e.g., compressed gas) is utilized to assist the migration of the electrolyte through the cartridge 40. The electrolyte becomes enriched with the chemical reagents 26, (*i.e.*, dissolved or suspended) while passing through the cartridge 40. The enriched electrolyte 29 accumulates near or at the headspace 49, and then proceeds to exit the cartridge 40 through the manifold 44. In one embodiment, the headspace 49 has enriched anolyte 29 as well as accumulated gas 46 or air. The accumulated gas 46 is bled from the headspace prior or during the flow of enriched anolyte 29. In another embodiment, a porous material (not shown), such as sponges, porous plastics, metals, ceramics, filters, frits, membranes, wool (e.g., glass or metal), packed inert

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

media (e.g., silica or alumina) and the alike is displaced below the manifold 44 to inhibit any large particulate of chemical reagents 26 from leaving the cartridge 40.

[0045] In another embodiment, Figure 7 shows a plating system 50 that includes a cartridge 40 of the invention. The enriched electrolyte 29 is added to anolyte tank 52, which is in fluid communication with an electroplating cell 56 and pump 58 within an anolyte loop. Anolyte is depleted of reagent chemical (e.g., Cu<sup>2+</sup> and OH<sup>-</sup>) during the plating process within the electroplating cell 56. Pump 58 drives the circulation of depleted anolyte to the anolyte tank 52 and enriched anolyte from the anolyte tank 52 to the electroplating cell 56.

[0046] A pH controller 54, pH sensor 57 and a computer 55 monitor and regulate the pH of the anolyte within the anolyte tank 52. A pH controller may be selected from a variety of commercially available models, such as dTRANSpH 01 from JUMO Process Control Inc., DP24-E Process Meter from Omega, EMIT-pH from Pathfinder Instruments, and LED pH/ORP indicator/controller from Kemko Instruments. In one embodiment, the pH is maintained in the range from about 1.0 to about 5.0, preferably, from about 2.0 to about 4.0 and more preferably from about 2.8 to about 3.0. In another embodiment, the pH is maintained at less than 3.4 to prevent chemical precipitants (e.g., copper hydroxide) from forming and clouding the anolyte.

[0047] As the pH of the anolyte becomes too low, an aliquot of the anolyte is transferred from anolyte tank 52 to canister 53 via three-way valve 60. Generally, three-way valve 61 is positioned to pressurize anolyte tank 52 with compressed gas (e.g., air) and three-way valve 60 is positioned as to accept the aliquot from the anolyte tank 52 to the canister 53. Once the aliquot is transferred, then both valves 60 and 61 are turned off. Subsequently, three way valve 61 is positioned to pressurize the canister 53 containing the aliquot of the anolyte while three-way valve 60 is positioned to permit the flow of the aliquot into the cartridge 40 via the injector 43. The enriched anolyte emerges from the cartridge 40 via the manifold 44 and into the anolyte tank 52. As the enriched anolyte combines with the depleted anolyte, acidic protons are neutralized by the incoming hydroxyl ions and copper

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

ions become more concentrated. In practice, the concentration of the anolyte will not vary much since control of the replenishment is occurring real time. That is, when valves 60 and 61 are timed and positioned correctly, the anolyte will reach a relatively constant pH with minimal flux (e.g., about 0.5 pH units). The compressed gas is delivered from a source 62, such as a tank or an in-house line and may include air, N<sub>2</sub>, Ar, He, H<sub>2</sub> and combinations thereof.

[0048] Figure 8 is a diagram illustrating a timing sequence of valves 60 and 61 during an electroplating process useful in the plating system 50 depicted in Figure 7. The timing of valves 60 and 61 is controlled by the pH controller 54 in combination with a computer 55. The valves 60 and 61 change positions every second or so and remain synchronized as described above. When the pH of the anolyte drops to a lower limit (LL), the compressed gas (e.g., air) moves the electrolyte from canister 53 into cartridge 40. The time  $t_1$  is slightly longer (e.g., about a second) than that required to push all of the anolyte from canister 53, so that a small amount of air also penetrates in to the cartridge 40. The air provides a thorough mixing of the chemical reagents with the anolyte and enriches the suspension (e.g., copper hydroxide) near the top of the cartridge 40 within headspace 49. This thorough mixing with the air and the conical shape of the bottom of the cartridge prevents cake formation. During time  $t_2$ , compressed air is stopped by closing valve 61 and canister 53 is refilled with anolyte through valve 60. During  $t_3$ , the anolyte is injected into cartridge 40 with the timing quick enough to prevent penetration of air into the canister 53, about a second. Canister 53 is refilled with anolyte that is subsequently injected into the cartridge 40. Thereafter, an enriched anolyte is transferred from the cartridge 40 to the anolyte tank 52. This cycle continues until the pH reaches a higher limit (HL), then ceases until the pH of the anolyte within the anolyte tank reaches the LL. The overall sequence repeats during the electroplating process.

[0049] In another embodiment, Figure 9 shows a plating system 70 that includes a cartridge 40. The enriched electrolyte 29 is added to anolyte tank 52, which is in fluid communication with an electroplating cell 56 and pump 58 within an anolyte loop. Anolyte is depleted of reagent chemical (e.g., Cu<sup>2+</sup> and OH<sup>-</sup>) during the plating

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

process within the electroplating cell 56. Pump 58 drives the circulation of depleted anolyte to the anolyte tank 52 and enriched anolyte from the anolyte tank 52 to the electroplating cell 56. The depleted anolyte is temporally contained within a section 71 of the anolyte tank 52. Section 71 is separated by partition 80 and will gather depleted anolyte as well as enriched anolyte, before flowing over into the main compartment of anolyte tank 52.

[0050] A pH controller 54, pH sensor 57 and a computer 55 monitors and regulates the pH of the anolyte within section 71. In one embodiment, the pH is maintained in the range from about 1.0 to about 5.0, preferably, from about 2.0 to about 4.0 and more preferably from about 2.8 to about 3.0. In another embodiment, the pH is maintained at less than 3.4 to prevent chemical precipitants (e.g., copper hydroxide) from forming and clouding the anolyte.

[0051] As the pH of the anolyte becomes too low, an aliquot of the anolyte is transferred from anolyte tank 52 to canister 53 via two-way valve 76. Pump 58 helps push the anolyte to canister 53. Once the aliquot is transferred, then two-way valve 72 is positioned to pressurize the canister 53 containing the aliquot of the anolyte while two-way valve 78 is positioned to permit the flow of the aliquot into the cartridge 40. The enriched anolyte flows from the cartridge 40 to section 71 of the anolyte tank 52. As the enriched anolyte combines with the depleted anolyte, acidic protons are neutralized by the incoming hydroxyl ions and copper ions become more concentrated. Two-way valve 74 is positioned open and gas flow agitates the enriched anolyte with the depleted with the flow of gas. In practice, the concentration of the anolyte will not vary much since the replenishment is occurring in real time. That is, when valves 72, 74, 76 and 78 are timed and positioned correctly, the anolyte will reach a relatively constant pH with minimal flux (e.g., about 0.5 pH units). The compressed gas is delivered from a source 62, such as a tank or an in-house line and may include air, N<sub>2</sub>, Ar, He, H<sub>2</sub> and combinations thereof.

[0052] In one embodiment depicted in Figure 10A, injector system 82 includes an injector 84 with output holes 85 and a cup 86 with output holes 87. Cup 86 is rotatable as to line-up the output holes 85 with output holes 87. Once lined-up,

PATENT

Attorney Docket No.: AMAT/8451/CMP/ECP/RKK  
Express Mail No.: EV351032102US

anolyte will pass through holes 85 and 87 and into the cartridge. To remove cartridge 40, output holes 85 and 87 are misaligned to turn off the excess of chemical reagents 26 from escaping the cartridge 40. Figure 10A illustrates cup 86 disposed within the injector 84, while in another embodiment, Figure 10B shows an injector 94 disposed within a cup 96 as part of injector system 92. Also, injector 94 contains output holes 95 and cup 96 contains output holes 97. The output holes 85 and 87 generally point horizontal while the output holes 95 and 97 point in a downwardly direction.

[0053] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.